



Short communication

Study of electrochemically active carbon, Ga₂O₃ and Bi₂O₃ as negative additives for valve-regulated lead-acid batteries working under high-rate, partial-state-of-charge conditions



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H I G H L I G H T S

- The sulfation of the negative plates was restrained by adding EAC in NAM.
- Ga₂O₃ or Bi₂O₃ decreased the evolution rate of hydrogen on EAC.
- The cut-off discharging voltage was increased by adding Ga₂O₃ or Bi₂O₃ in NAM.
- The life of batteries was prolonged for 3 times by adding 0.01% Ga₂O₃ in NAM.

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Electrochemically active carbon (EAC), Gallium (III) oxide (Ga₂O₃) and Bismuth (III) oxide (Bi₂O₃) are used as the negative additives of valve-regulated lead-acid (VRLA) batteries to prolong the cycle life of VRLA batteries under high-rate partial-state-of-charge (HRPSoC) conditions, and their effects on the cycle life of VRLA batteries are investigated. It is found that the addition of EAC in negative active material can restrain the sulfation of the negative plates and prolong the cycle performance of VRLA batteries under HRPSoC conditions. It is also observed that the addition of Ga₂O₃ or Bi₂O₃ in EAC can effectively increase the overpotential of hydrogen evolution on EAC electrodes, and decrease the evolution rate of hydrogen. An appropriate addition amount of Ga₂O₃ or Bi₂O₃ in the negative plates of VRLA batteries can decrease the cut-off charging voltage, increase the cut-off discharging voltage, and prolong the cycle life of VRLA batteries under HRPSoC conditions. The battery added with 0.5% EAC and 0.01% Ga₂O₃ in negative active material shows a lowest cut-off charging voltage and a highest cut-off discharging voltage under HRPSoC conditions, and its' cycle life reaches about 8100 cycles which is at least three times longer than that without Ga₂O₃.

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1. Introduction

Electric vehicles (EVs) and fuel-cell vehicles are the future transports, but these vehicles are still under development and improvement. In the short to medium term, hybrid electric vehicles (EVs) are generally regarded as having the greatest potential for improving air quality, since they offer significantly improved emissions performance without operational restrictions [1]. The battery in the above HEVs is charged and discharged at a very high frequency under high-rate partial-state-of-charge (HRPSoC)

conditions. High-rate discharge is necessary for engine cranking and acceleration, while high-rate charge is associated with regenerative braking [2]. That means the charge and discharge process involves only a small fraction of the battery's capacity, but they occur continuously and do take place at a very high rate [3,4]. Valve-regulated lead-acid (VRLA) battery is considered one of the candidate energy-storage systems for HEVs applications because of its low initial cost and high recycling efficiency [5–7]. Nevertheless, VRLA batteries operating under HRPSoC conditions will result in irreversible formation of lead sulfate in negative plates [2,8,9]. VRLA batteries in HRPSoC cycling typically fail because of heavy sulfation of negative plates, accompanied by higher internal resistance and cell dry out [10].

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Based upon the above failure mechanism of VRLA batteries [11], Nakamura et al. put forward that the addition of carbon materials into the negative-active-mass (NAM) of VRLA batteries could restrain the sulfation of negative plates [12,13]. The use of carbon minimizes the uneven distribution of lead sulfate within the cross-section of negative plate, reduces discharge and charge current densities, and provides conductive network to facilitate subsequent charging process [14,15]. Carbon materials in H_2SO_4 solution can also act as a double-layer capacitor electrode, which serves as a buffer to share the charge and discharge currents with the lead-acid negative plates and thus prevents it being discharged and charged at the high rates required by the HEV duty [16]. So carbon materials are helpful for enhancing the cycle performance of the negative plates under HRPSOC conditions [17,18].

Although the addition of carbon materials in negative plates can restrain lead sulfate crystal's growth and share the charge and discharge currents with the lead-acid negative plates, it will increase the evolution rate of hydrogen on negative plates during charging process. Toward the end of charge, the carbon materials in negative plates will evolve significant hydrogen gas than the lead negative plates because its potential now is shifted to a more negative value than it should be [19], which negatively influences the cycle performance of battery. Therefore, it is necessary to reduce the hydrogen evolution rate on carbon materials during charging process.

In this paper, electrochemically active carbon (EAC) [20] was used as the added carbon material in VRLA batteries, and Ga_2O_3 and Bi_2O_3 were used as negative additives for the purpose of inhibiting the hydrogen evolution on EAC and prolonging the HRPSOC cycle life of VRLA batteries.

2. Experimental

2.1. Preparation of negative plates

In our investigation, EAC negative electrodes and the negative plates of VRLA batteries were prepared, respectively. EAC negative electrodes were prepared by filling EAC (90%), acetylene black (10%) and different amounts of Ga_2O_3 or Bi_2O_3 with CMC binder into $1\text{ cm} \times 1\text{ cm}$ Pb–Ca grids. The content of Ga_2O_3 or Bi_2O_3 was varied from 0% to 8% of the mass of EAC and acetylene black. Negative plates of VRLA batteries were prepared by using lead oxide powder, barium sulfate, humic acids, and different amounts of EAC and Ga_2O_3 or Bi_2O_3 . The content of EAC was varied from 0% to 2%, and the additive amounts of Ga_2O_3 or Bi_2O_3 were 0%, 0.005%, 0.01%, 0.02% and 0.04%, respectively.

2.2. Performance measurements

The effects of Ga_2O_3 and Bi_2O_3 on the evolution rate of hydrogen on EAC in H_2SO_4 solution were studied by using linear sweep voltammetric method. A prepared negative plate was used as working electrode, a commercial PbO_2 positive plate and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode were used as counter electrode and reference electrode, respectively. H_2SO_4 solution with a density of 1.347 g cm^{-3} was used as electrolyte. The measuring equipment was a CHI630A electrochemical workstation made by CH Instruments Inc. The scanning range was 0 to -1.50 V , and scanning rate was 5 mV s^{-1} .

The effects of Ga_2O_3 and Bi_2O_3 on the cycle performance of VRLA batteries under HRPSOC conditions were investigated by using charge/discharge method. Test cells were assembled from two commercial positive plates and one negative plate which was prepared in 2.1. The thickness of the negative plate and the positive plate were 2 mm and 2.5 mm, respectively. H_2SO_4 solution with a density of 1.347 g cm^{-3} was used as the electrolyte. The initial

capacity of the test cell was about 1.5 Ah, which was decided by the capacity of the negative plate. Cycle performance under HRPSOC conditions was tested by using a BTS series battery testing system made by Neware Technology Limited. After being activated, the test cells were firstly discharged to 50% of their initial capacity at 1C and then cycled as follows: Charge at 2C rate for 60 s, stand for 60 s, discharge at 2C rate for 60 s, stand for 60 s. The test process was terminated automatically when the cut-off discharging voltage of the test cells fell down to 1.60 V or the cut-off charging voltage increased to 2.90 V.

The surface morphologies and microstructures of the negative plates were observed at a voltage of 20 kV using a Hitachi S4700 scanning electron microscope.

3. Results and discussions

3.1. Cycle performance of VRLA battery added with different amounts of EAC

HEVs require the battery to be charged and discharged under HRPSOC conditions, so the effect of EAC on cycle performance of VRLA battery under HRPSOC conditions was investigated in this study. Fig. 1 presents the effects of EAC on the cycle performance of VRLA battery under HRPSOC conditions.

It can be seen from Fig. 1 that the content of EAC in the negative plates has a crucial influence on the cut-off charging/discharging voltages of batteries: the cut-off charging voltages of different batteries vary from 2.2 V to 2.9 V, and the cut-off discharging voltages vary from 1.6 V to 2.0 V. The cut-off charging voltage increases rapidly in the early stage of cycle test, then stabilizes at a certain range, and the cut-off discharging voltage decreases gradually with the increase of cycle number. The addition of EAC in negative plates can decrease the charge potential, increase the discharge potential (after 800–1000 cycles), and enhance the HRPSOC cycle performance of VRLA batteries obviously. The cycle life of VRLA batteries under HRPSOC conditions can be prolonged about 1000 cycles by adding 0.5–2% EAC in negative plates.

The presence of EAC in negative plates can improve the dispersion of the active substances, restrain the growth and deactivation of lead sulfate crystals, and enhance the utilization of active substances and cycle life of batteries. On the other hand, when the battery was charged or discharged, EAC in negative plates could supply double-layer capacitance. It could also weaken the damage of negative plates caused by high current density with the buffer action, which is helpful for prolonging the cycle performance of negative plates [16]. It should be noted that, although EAC can

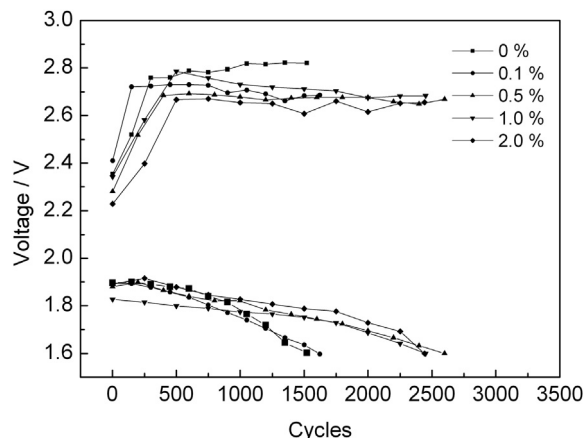


Fig. 1. Effect of EAC on cycle performance of VRLA batteries under HRPSOC conditions.

restrain the sulfation of negative plates, its addition amount should be controlled in a suitable range. Excessive EAC in negative plates will increase the evolution rate of hydrogen on negative plates in charging process, accelerate the water loss of battery, and furthermore shorten the cycle life of battery.

According to Fig. 1, although the cycle life of batteries varied with the addition amount of EAC in negative plates, the reasons that the cycle tests were terminated automatically for all batteries are same: the cut-off discharge voltage decreased to 1.60 V (the setting lowest limit voltage). Because the charge/discharge process of cycle life test is: charge at 2C rate for 60 s, then discharge at 2C rate for 60 s, the battery with a higher charge acceptance will be charged more effective electric quantity, and it will show a higher cut-off discharging voltage at the end of discharge process. In our study, the battery was assembled with one negative plate and two positive plates, the battery capacity was limited by the negative plate. So it can be concluded from Fig. 1 that the addition amount of EAC in negative plates can affect the cycle performance of batteries under HRPSOC conditions by means of affecting the charge acceptance of negative plates.

In order to well understand the effect of EAC on the cycle performance of the negative plates, the surface morphologies and microstructures of the negative plates were observed after the cycle tests were terminated automatically. Fig. 2 presents SEM micrographs of the negative plates containing 0%, 0.1%, 0.5% and 2.0% EAC, respectively. Because the negative plates were in discharge state, the principal component of the negative plates was PbSO_4 . It can be seen from Fig. 2 that, the negative plate without EAC constructed with some relatively smooth PbSO_4 particles. With the increase of

addition amounts of EAC, PbSO_4 particles become rough and loose, but excessive addition amounts of EAC promoted the aggregation of PbSO_4 particles. So it can be concluded that appropriate addition amounts of EAC in NAM can restrain the sulfation of negative plates. The porosity and the acid-affinity characteristics of EAC provide many acid reservoirs within the interior of the plate and these reservoirs give rise to active sites for the development of lead sulfate during discharge [11]. On the other hand, the EAC can act as a buffer to share the discharge and charge currents with the lead acid negative plate and thus, prevents it being discharged and charged at the high rates. So the sulfation of negative plates can be restrained.

3.2. Effect of Ga_2O_3 on the hydrogen evolution rate of EAC

Addition of EAC into NAM can restrain the sulfation of the negative plates, but it will lead to another undesired problem. EAC added in negative plates acts as a carbon-based capacitor electrode in VRLA battery. During charging, the charge current will flow to the capacitor electrode first and then to the lead-acid negative plate. Toward the end of charge, however, the capacitor electrode will evolve significant hydrogen gas than the lead negative-plate because its potential now is shifted to a more negative value than it should be [2]. Hydrogen evolution is a harmful side-reaction for VRLA batteries, and it will cause the electrolyte dry-out of the battery. In order to decrease the hydrogen evolution rate of EAC in H_2SO_4 solution during charging process, high hydrogen evolution overpotential materials were added into EAC in this study. Metallic Ga is a kind of high hydrogen evolution overpotential material, but its low

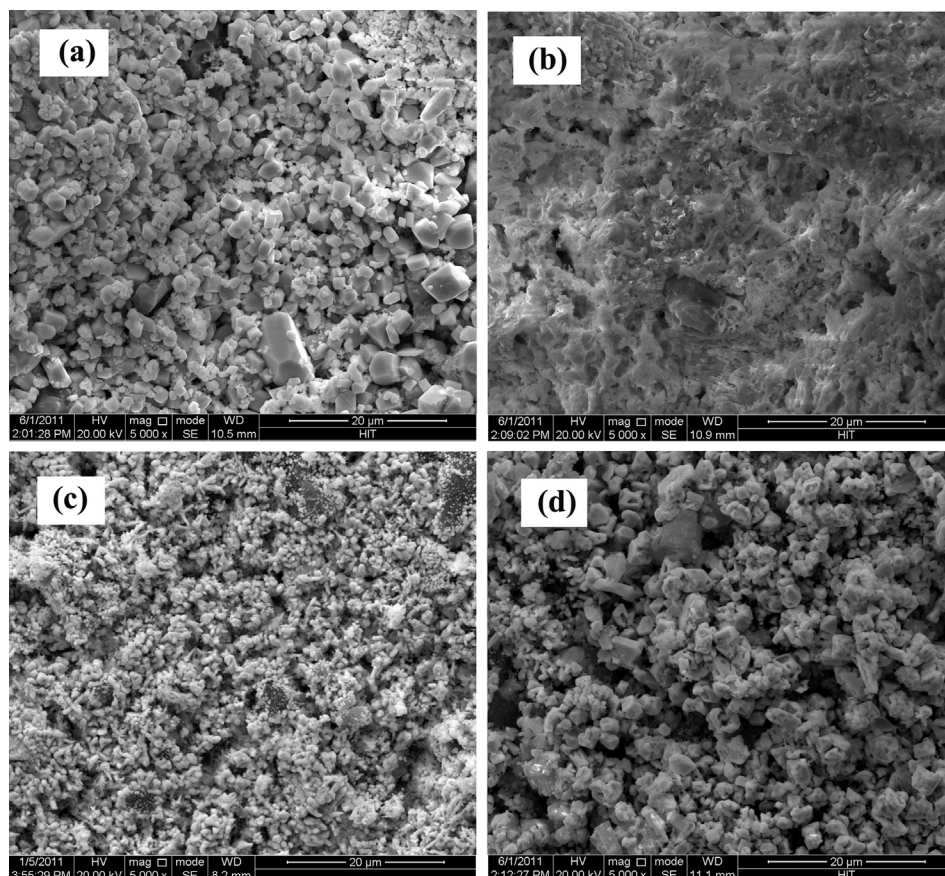


Fig. 2. SEM photos of negative plates added with different amounts of EAC, after the cycle test was finished: (a) 0%, (b) 0.1%, (c) 0.5%, (d) 2.0%.

melting point constrains its direct application in preparing negative electrode. According to the Pourbaix diagram of Ga–H₂O system [21], Ga₂O₃ is unstable in our experimental conditions, it will exist in metallic Ga form in negative electrode. So as one of the candidate materials, Ga₂O₃ was added into EAC. Effect of addition amounts of Ga₂O₃ on the cathodic polarization curve of EAC in H₂SO₄ solution is given in Fig. 3. A current peak was observed at the potential range of –1.16 to –1.18 V, which corresponds to the reduction reaction of PbSO₄ (produced by the dissolution of grids in H₂SO₄ solution) to Pb [22]. In other potential range, the responding current consists of two parts: current of double layer charge and current of hydrogen evolution. In our measurement conditions, the current of double layer charge for each electrode is almost the same, so the current difference for each electrode in Fig. 3 mostly results from the difference of hydrogen evolution current. It can be seen from Fig. 3 that addition of Ga₂O₃ in EAC influenced the hydrogen evolution rate on EAC. At a given potential, the hydrogen evolves more on the EAC electrode without Ga₂O₃ than on the EAC electrode with Ga₂O₃. With increasing Ga₂O₃ content in EAC, the hydrogen evolution rate decreased initially, and then increased. The minimum hydrogen evolution rate was obtained when addition amount of Ga₂O₃ in EAC equals 2%. Too much addition of Ga₂O₃ will increase the hydrogen evolution rate on EAC because of the negative catalysis effect [23].

3.3. Effect of Bi₂O₃ on the hydrogen evolution rate of EAC

As another type of high hydrogen evolution overpotential material, Bi₂O₃ was added into the EAC of VRLA battery with the purpose of decreasing the hydrogen evolution rate on EAC in H₂SO₄ solution during cathodic process. Effect of addition amounts of Bi₂O₃ on the cathodic polarization curve of EAC in H₂SO₄ solution is given in Fig. 4. The current peak observed at the potential range of –1.16 to –1.18 V corresponds to the reaction of PbSO₄ to Pb. It can be seen from Fig. 4 that with the increase of Bi₂O₃ content in EAC, the hydrogen evolution rate gradually decreased. EAC added with 4% and 8% Bi₂O₃ exhibited almost the same hydrogen evolution rate, so the appropriate addition amount of Bi₂O₃ in EAC should be 4% for the consideration of prime cost.

Although Ga₂O₃ or Bi₂O₃ added in EAC can decrease the hydrogen evolution rate of EAC in H₂SO₄ solution, they exhibited different effect principles. So the problem of which one is more suitable for the negative plate can only be solved by the following performance tests of batteries.

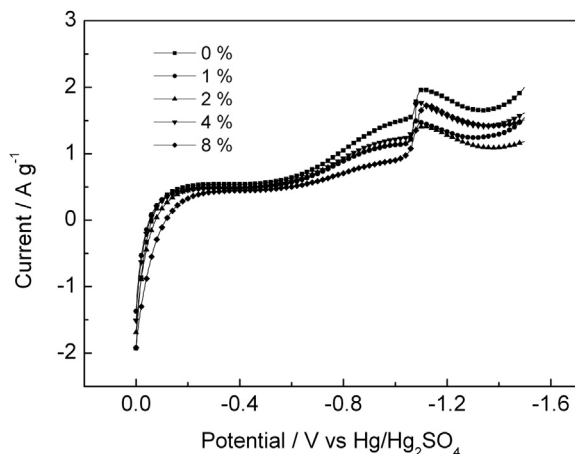


Fig. 3. Cathodic polarization curves of EAC added with different amounts of Ga₂O₃ at a scan rate of 5 mV s⁻¹.

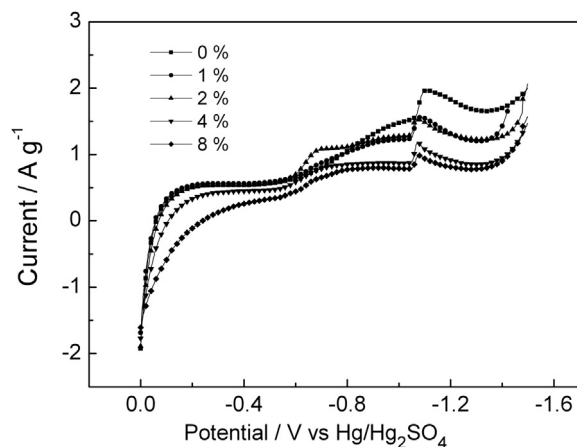


Fig. 4. Cathodic polarization curves of EAC added with different amounts of Bi₂O₃ at a scan rate of 5 mV s⁻¹.

3.4. Effect of Ga₂O₃ on cycle performance of VRLA batteries under HRPSoc conditions

Corresponding to the content of Ga₂O₃ in EAC in Fig. 3, different amounts of Ga₂O₃ (0%, 0.005%, 0.01%, 0.02% and 0.04%) together with 0.5% EAC were added into the NAM to prepare individual VRLA batteries, and the cycle performance of VRLA batteries under HRPSoc conditions were tested. Fig. 5 shows the cut-off charging/discharging voltages of the prepared VRLA batteries during HRPSoc cycles.

It can be seen from Fig. 5 that the content of Ga₂O₃ in the negative plates has a crucial influence on the cut-off charging/discharging voltages of batteries. The cut-off charging voltages of all batteries increased rapidly in initial stage, then remained unchanged at a certain range. Different batteries showed different stable cut-off charging voltage, and the battery with 0.01% Ga₂O₃ addition in NAM showed a lowest cut-off charging voltage. The cut-off charging voltages of all the tested batteries did not reach the highest setting limit of voltage 2.90 V during the whole testing process. It also can be seen from Fig. 5 that, the cut-off discharging voltages of all batteries decreased gradually with increase of cycle number, and finally decreased to the lowest setting limit of voltage 1.60 V. According to the charge/discharge mode of cycle life test, the electric quantity of charge and discharge is equivalent for a battery

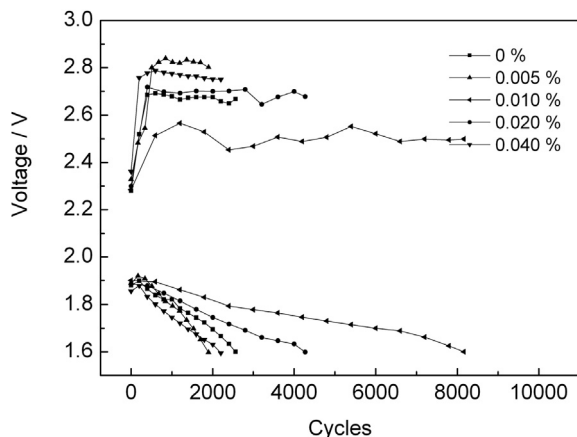


Fig. 5. Cut-off charging/discharging voltage of batteries contained different amounts of Ga₂O₃ in NAM during cycle test process.

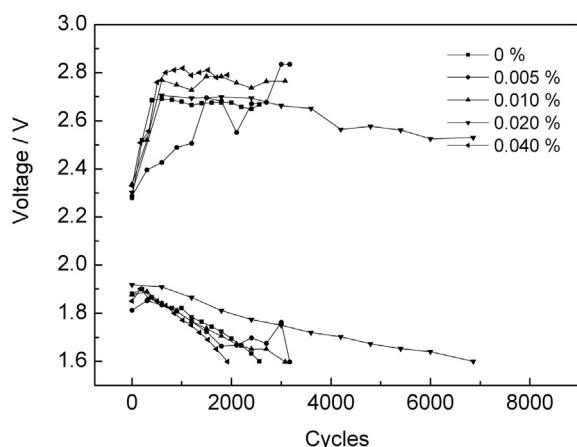


Fig. 6. Cut-off charging/discharging voltage of batteries contained different amounts of Bi_2O_3 in NAM during cycle test process.

in a single cycle. The charge acceptance of a battery is one of the most important factors influencing the cut-off discharging voltage of battery. The battery with a higher charge acceptance could be charged more effective electric quantity, and it thus shows a higher cut-off discharging voltage at the end of the discharge process. In our study, the battery was assembled with one negative plate and two positive plates, the battery capacity was limited by the negative plate, so the charge acceptance of a battery is relative to the evolution rate of hydrogen on negative plate. A lower hydrogen evolution rate means less current into gassing and more current into the charging reaction. So a lower hydrogen evolution rate will lead to a higher charge acceptance. The battery with 0.01% Ga_2O_3 addition in NAM showed a lowest cut-off charging voltage and a highest cut-off discharging voltage, therefore, it can be concluded that the battery with 0.01% Ga_2O_3 addition in NAM had a highest charge acceptance.

It also can be found from Fig. 5 that, Ga_2O_3 in the negative plates exerts a considerable influence on the cycle life of VRLA batteries under HRPSoc conditions. An appropriate addition amount of Ga_2O_3 in negative plates can prolong the cycle life of batteries, whereas too little or excessive Ga_2O_3 in negative plates was harmful to HRPSoc cycle performance of VRLA batteries. The battery containing 0.01% Ga_2O_3 in NAM, which corresponding to 2% Ga_2O_3 in EAC, attained the longest cycle life (nearly 8200 cycles), which is 3 times longer than that of the battery without Ga_2O_3 ; its cut-off discharging voltage was permanently higher than that of the other batteries. Therefore it can be concluded that an appropriate amount of Ga_2O_3 in the negative plates can inhibit evolution of hydrogen during the charge process, and enhance the charge acceptance and cycle performance of batteries under HRPSoc conditions.

3.5. Effect of Bi_2O_3 on cycle performance of VRLA batteries under HRPSoc conditions

In order to investigate the effect of Bi_2O_3 on the cycle performance of VRLA batteries under HRPSoc conditions, different amounts of Bi_2O_3 (0%, 0.005%, 0.01%, 0.02% and 0.04%) together with 0.5% EAC were added into the NAM to prepare individual VRLA batteries. Fig. 6 shows the cut-off charging/discharging voltages of

the prepared VRLA batteries during HRPSoc cycles. It can be seen from Fig. 6 that the content of Bi_2O_3 in the negative plates exerts a great influence on the cut-off charging/discharging voltages and cycle life of batteries. The battery with 0.02% Bi_2O_3 addition in NAM (corresponding to 4% Bi_2O_3 in EAC) showed a highest cut-off discharging voltage and a lower cut-off charging voltage, and its cycle life reached 6800 cycles, which is 2.6 times longer than that of the battery without Bi_2O_3 .

It can be concluded from the comparison of Figs. 5 and 6 that the battery containing 0.01% Ga_2O_3 in NAM showed the longest cycle life under HRPSoc conditions.

4. Conclusions

The cycle life of VRLA batteries under HRPSoc conditions can be prolonged by the addition of EAC in negative active material, because EAC can restrain the sulfation of the negative plates. The addition of Ga_2O_3 or Bi_2O_3 in EAC can effectively decrease the hydrogen evolution rate on EAC during cathodic process. An appropriate addition amount of Ga_2O_3 or Bi_2O_3 in the negative plates of VRLA batteries can decrease the cut-off charging voltage, and increase the cut-off discharging voltage of VRLA batteries under HRPSoc conditions. By comparison with Bi_2O_3 , Ga_2O_3 is a more effective type of additive for the negative plates of VRLA batteries. The battery added with 0.5% EAC and 0.01% Ga_2O_3 in negative active materials exhibits at least three times longer cycle life than that without Ga_2O_3 .

References

- [1] A. Cooper, J. Power Sources 133 (2004) 116–125.
- [2] L.T. Lam, R. Louey, J. Power Sources 158 (2006) 1140–1148.
- [3] J. Furukawa, T. Takada, D. Monma, L.T. Lam, J. Power Sources 195 (2010) 1241–1245.
- [4] P.T. Moseley, J. Power Sources 191 (2009) 134–138.
- [5] J. Albers, E. Meissner, S. Shirazi, J. Power Sources 196 (2011) 3993–4002.
- [6] D. Pech, T. Brousse, D. Bélanger, D. Guay, Electrochim. Acta 54 (2009) 7382–7388.
- [7] H. Li, H.P. Liu, Q.M. Wang, H.Y. Chen, A.F. Ren, J.G. Hu, Electrochim. Acta 56 (2010) 663–666.
- [8] L.T. Lam, N.P. Haigh, C.G. Phyland, A.J. Urban, J. Power Sources 133 (2004) 126–134.
- [9] L.T. Lam, N.P. Haigh, C.G. Phyland, T.D. Huynh, J. Power Sources 144 (2005) 552–559.
- [10] K.R. Bullock, J. Power Sources 195 (2010) 4513–4519.
- [11] L.T. Lam, R. Louey, N.P. Haigh, O.V. Lim, D.G. Vella, C.G. Phyland, L.H. Vu, J. Furukawa, T. Takada, D. Monma, T. Kano, J. Power Sources 174 (2007) 16–29.
- [12] K. Nakamura, M. Shiomi, K. Takahashi, M. Tsubota, J. Power Sources 59 (1996) 153–157.
- [13] M. Calabek, K. Micka, P. Krivak, P. Baca, J. Power Sources 158 (2006) 864–867.
- [14] M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota, J. Power Sources 64 (1997) 147–152.
- [15] D. Pavlov, P. Nikolov, T. Rogachev, J. Power Sources 195 (2010) 4444–4457.
- [16] A. Cooper, J. Furukawa, L. Lam, M. Kellaway, J. Power Sources 188 (2009) 642–649.
- [17] L.T. Lam, R.H. Newnham, H. Ozgun, F.A. Fleming, J. Power Sources 88 (2000) 92–97.
- [18] M. Fernández, J. Valenciano, F. Trinidad, N. Muñoz, J. Power Sources 195 (2010) 4458–4469.
- [19] Y. Chen, B.Z. Chen, X.C. Shi, H. Xu, W. Shang, Y. Yuan, L.P. Xiao, Electrochim. Acta 53 (2008) 2245–2249.
- [20] D. Pavlov, T. Rogachev, P. Nikolov, G. Petkova, J. Power Sources 191 (2009) 58–75.
- [21] J. Price, J. Barnett, S. Raghavan, M. Keswani, R. Govindarajan, Microelectron. Eng. 87 (2010) 1661–1664.
- [22] B. Rezaei, M. Taki, J. Solid State Electrochem. 12 (2008) 1663–1671.
- [23] Y.X. Chen, Q.S. Zhang, Z.M. Yu, Battery Bimon. 5 (1997) 195–198.